PATENT

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METHOD FOR DOMAIN PATTERNING IN LOW COERCIVE FIELD FERROELECTRICS

Field of the Invention:

The invention relates to Ferroelectric materials. More specifically, the invention relates to Ferroelectric materials with patterned domain structures.

Background of Invention:

Nonlinear materials are used in a variety of technologies including data storage, display and communications technologies. Nonlinear materials and their effects with interacting electromagnetic radiation is well documented. Nonlinear materials are used as harmonic generators. Most commonly, nonlinear materials are used to generated the second harmonic emission light wave λ_e of an interacting light source with a fundamental wavelength λ_i. Figure 1, for example, shows a single pass second harmonic generator construction 100. A solid state infrared laser 101 emits light with a fundamental wavelength 107. The light wave 107 is focused with a confocal lense 103 on a crystal 104 that is formed from a nonlinear material. The emission second harmonic wavelength 109 is half of the fundamental wavelength 107; equivocally the second harmonic output frequency is twice that of the fundamental input frequency. The nonlinear crystal 104 needs to be transparent to incident light with a wavelength 107 so that the light wave 107 can propagate through the crystal 104. Further, the crystal 104 needs to be transparent the to second harmonic light with a wavelength 109 so that the second harmonic light wave 109 is emitted from the crystal 104.

There are several factors that lead to inefficient conversion of the fundamental wave length 107 to the second harmonic wavelength 109. Specifically, low nonlinear coefficient of crystal material, defects in the crystal structure, low transparency of the nonlinear material, and

other geometric considerations of the crystal can all lead to inefficient conversion of the fundamental wavelength 107 to the second harmonic wavelength 109. A crystal structure that is made from a material with a small nonlinear coefficient can in theory be compensated for by increasing the crystal pass length L. In practice, however, local defects and variations in refractive index throughout the crystal 104 begin to diminish any benefits gained from extending the crystal path length.

Even when the crystal 104 is formed from a material that exhibits a large nonlinear coefficient, the actual observed conversion efficiency of the fundamental wavelength 107 to its corresponding harmonic wavelength 109 is typically low. This is because light with a wavelength 107 and 109 exhibits different indices of refraction within the crystal 104. Hence, the fundamental wavelength 107 and the harmonic wavelength 109 have different phase velocities as they propagate through the crystal 104. Consequently, as the second harmonic wave 109 is locally generated in one portion of the crystal, it will be out of phase with the fundamental wavelength 107 and with the second harmonic wave 109 that is locally generated in a later part of the crystal 104 resulting in destructive interference and low output of the second harmonic light. To help overcome this problem, nonlinear materials are modified. Nonlinear materials are modified either so that the phase velocities of λ_e and λ_i are matched, a method referred to a bifringent phase matching, or alternatively the nonlinear materials are modified such that the sign of the nonlinear coefficient is periodically modulated by a distance corresponding to the coherence length of the light, a method referred to a quasi-phase matching (QPM) and described in an early work by J. A. Armstrong, N. Bloembergen, J. Ducuing and P.S. Pershan in "Interaction Between Light Waves in a Nonlinear Dielectric," Phys. Rev., 127, 1918, 1962.

QPM is a method which compensates for the differences in the phase velocity between the fundamental wavelength of the interacting light source and the corresponding harmonic wavelength within the nonlinear crystal. In quasi-phase matching, the fundamental wave and the harmonic wave still have different phase velocities, but they are shifted π out of phase relative to one another over the coherence length. The coherence length is used to refer to the distance over which two traveling waves slip out of phase by π radians. The sign of the non-linear coefficient is reversed once every coherence length (or odd multiples of coherence lengths) causing a locally

generated harmonic field within the nonlinear structure to transfer power to the harmonic beam. By compensating for the phase velocity mismatch between the fundamental wave and the harmonic wave in this way, all the elements of the crystal nonlinear tensor can be accessed throughout the entire transparency range of the crystal. This invention is directed to improved materials and methods for making quasi-phase matching structures preferably for use in non-linear optics.

Summary of the Invention:

The invention provides a method for domain patterning of nonlinear Ferroelectric materials. The method is particularly useful for domain patterning of Ferroelectric structures which exhibit low coercive fields and which exhibit charging with small changes in temperature. The method seeks to reduce the formation of random micro-domains that typically result during thermal cycling of Ferroelectric materials and which lead to patterning defects and reduced efficiencies. According to the preferred method of the invention, a Ferroelectric structure is provided with conductive layers on the top surface and the bottom surface of the structure which correspond to surfaces that are normal to the crystallographic polarization axis or z-polarization vectors. The conductive layer is a conductive polymer, a metal layer or a layer of conductive polymer composition. Preferably, the conductive layers are formed from a mixture of polyaniline salt, n–Methyl pyrrolidone and Isopropanol, available under the name of ORMECON™ D-1000 manufactured by Ormecon Chemie GmbH & Co. KG, Ferdinand-Harten-Str. 7, D-22949, Ammersbek, Germany.

A mask is provided over a patterning surface of the structure. For simplicity, the patterning surface is referred to herein as the top surface of the structure. The mask preferably substantially replicates the intended domain pattern. Portions of the conductive layer on the top surface of the structure are removed in accordance with the pattern of the mask, thus leaving a conductive domain template on the top surface of the structure. Subsequently, a sufficient bias voltage is applied to the conductive domain template and the conductive layer on the bottom surface of the structure, thereby producing a domain patterned Ferroelectric structure. The conductive layer, the mask and the conductive domain template are then preferably removed

from the structure. The resulting domain patterned Ferroelectric structure is then relatively stable against charging effects due to temperature variations. A final protective conductive coating may be applied to provide additional long-term stability of the domain pattern.

The mask is preferably provided by lithographic techniques by using lithographic materials. Accordingly, a portion of the conductive layer on the top surface of the Ferroelectric structure is coated with a photo-resist such by any suitable method. After the photo-resist is coated on the top conductive layer, the photo-resist is thermal cycled in accordance with the manufacturer's recommendations. The photo-resist is then exposed according to a predetermined pattern with a suitable light source and developed to form the mask.

During thermal cycling of the photo-resist, charging on the surfaces of the Ferroelectric typically occurs leading to electron emission and random domain formation during cooling. In order to mitigate the charging of the structure during thermal cycling of photo-resist, it is preferable that the conductive layers on the top surface and the bottom surface are placed in electrical communication prior to thermal cycling, thus reducing the charging. The top and bottom conductive layers are preferably placed in electrical communication by providing a conductive layer to a side surface of the Ferroelectric structure.

After the mask is formed and prior to creating the domain patterning, the conductive layer on the top and bottom surfaces of the structure is placed in electrical isolation by removing the conductive layer from the side surface of the structure and applying a sufficient bias voltage across the top and bottom conductive layers. This urges the Ferroelectric structure to assume a single domain structure, wherein the signs of the polarization vectors are in one direction throughout the structure. The voltage that is required to uniformly polarize the structure depends on the Ferroelectric material used, but is approximately 21 KV/mm or less for many Ferroelectric materials and is defined by the coercive field Ec of the material used to form the structure and the thickness of the structure.

After the mask is formed and the structure is uniformly polarized, portions of the conductive layer on the top surface are removed in accordance with the mask to form a conductive domain template. A sufficient reverse bias voltage is then applied across the conductive domain template and the conductive layer on the bottom surface of the Ferroelectric

structure causing the regions of the structure between the domain template and the conductive layer on the bottom surface to reverse their polarization, thereby creating the domain patterning throughout the Ferroelectric structure.

The Ferroelectric structure is preferably formed from $LiNbO_3$, $KTiOPO_4$ and $LiTaO_3$. Most preferably, the Ferroelectric structure is a stoichiometric $LiNbO_3$ or $LiTaO_3$ wafer which exhibits a low coercive field. Further, the domain patterned Ferroelectric structure is preferably a quasi-phase matching structure wherein the domains are spatially modulated by a distance corresponding to a coherence length required for generating a harmonic emission wave form with a wavelength λ_e from a fundamental wave form of an interacting light source with a wavelength λ_i.

A harmonic generator for generating a harmonic emission wave form utilizes the quasi-phase matching structure of the instant invention formed from a Ferroelectric material which exhibits spontaneous reversal of local polarizations by changes in temperature ΔT between 0.1 and 40 degrees, wherein $\Delta T_{,}= q^{-1} \cdot \xi \cdot E_c$, q is the pyroelectric coefficient, ξ is the permitivity of the Ferroelectric and E_c is the coercive field. An interacting light source, with the fundamental wavelength λ_i is configured to be incident with the quasi-phase matching structure such that a portion of the light with the wavelength λ_i interacts with the quasi-phase matching structure generating the harmonic emission wave form with a wavelength λ_e.

Brief Description of the Drawing:

Figure 1 is a schematic representation of a harmonic generator.

Figure 2 is a schematic representation of a periodically poled nonlinear structure.

Figure 3 is a block flow diagram outlining the method for making a periodic domain patterned Ferroelectric structure in accordance with the invention.

Figure 4a-g illustrates the steps of making a periodic domain patterned Ferroelectric structure according to the preferred embodiment of the invention.

Figure 5 shows a structure with domain patterning on a high coercive field Ferroelectric

Figure 6 shows a structure with domain patterning on a low coercive field Ferroelectric.

Detailed Description of the Invention:

In general, the present invention is for domain patterning of Ferroelectric materials used in nonlinear optics and related applications. Ferroelectric materials such as $LiNbO_3$, $KTiOPO_4$ and $LiTaO_3$ have been implicated as suitable candidates in QPM structures. When exposed to sufficient changes in temperature, Ferroelectric materials produce a surface charge. The surface charge gives rise to an electric field having a component that is parallel to the polar axis of the Ferroelectric material. This phenomenon is called the pyroelectric effect. Some Ferroelectric materials such as $LiNbO_3$ and $LiTaO_3$, produce a surface charge that produces such an anti-polar electric field during cooling, while other materials produce an anti-polar electric field during heating, both of which can lead to spontaneous reversal in the sign of the local polarization vector. This spontaneous reversal in the sign of the local polarization vector produces random micro domains in the structure. The process of reversing the sign of the local polarization vector is referred to as poling. The change in temperature that is required to cause the spontaneous reversal of the local polarization is given by $\Delta T = q^{-1} \cdot \xi \cdot E_c$, where q is the pyroelectric coefficient, ξ is the permitivity of the Ferroelectric and E_c is the coercive field. In congruent lithium tanatlate, for example, an anti-polar field sufficient to cause the sign of polarization vectors to spontaneously switch is generated at a ΔT of approximately 50 degrees Kelvin, wherein the coercive field value of the material is 21 kV/mm. In commercially available stoichiometric lithium tanatlate, such as available by Oxide Corporation, 9633 Kobuchizawa, Kitakoma, Yamanashi, 408-0044 Japan, the coercive field is much lower, approximately 1.7 kV/mm. This lower coercive field reduces the temperature decrease that results in poling to approximately 4.0 degrees.

To achieve periodic domain inversion or domain patterning on the surfaces of Ferroelectric materials, dopant infusion has been employed; for example, see E. J. Lim, M. M. Fejer, and R. L. Byer, "Second-Harmonic Generation of Green Light in Periodically Poled Planar Lithium Niobate Waveguides," Electronics Letters, 25 (3), pp. 174-175, 1989. In order to achieve bulk periodic domain formation, lithographic techniques have been employed, whereby the domains are defined by lithographic techniques and a sufficient electric field is applied to the Ferroelectric material to cause inversion of the nonlinear coefficient. For early work describing

using lithographic techniques for domain patterning, see M. Yamamada, N. Nada, M.. Saitoh et al., "First Order Quasi-Phase Matched $LiNbO_3$ waveguide Periodically Poled by Applying an External Field for Efficient Blue Second-Harmonic Generation," Applied Physics Letters, 62 (5), pp. 435-436, 1993.

Unfortunately Lithographic processes and other wafer processing steps typically involve thermal cycling ΔT that can be on the order of 100 degrees or more and can readily result in the formation of random micro-domains. The formation of random micro domains in the Ferroelectric material results in defects in subsequently produced domain patterned structures and degrades the performance of the QPM device produced therefrom. Therefore, there is a need for an improved method for making periodic domain patterned structures from Ferroelectric materials, wherein high resolution domain patterning is achieved using lithographic techniques, but where the formation of random micro domains is reduced during thermal cycling processes.

Per the above equation, spontaneous poling or micro domain formation is even more problematic for low coercive field Ferromagnetic materials. A Stoichiometric $LiNbO_3$ or $LiTaO_3$ wafer exhibits a low coercive field value which can be as low as 1/100 of that of the parent wafer or less. Consequently, spontaneous local reversal of sign of polarization vectors can occur at a fraction of the ΔT observed for conventional congruently grown wafers.

There are several potential advantages to using these low coercive field Ferroelectric materials. In some Ferroelectric materials, a lowered coercive field can result in substantial improvement in domain patterning. Further, some domain patterned low coercive field materials show good optical stability.

Figure 2 is a schematic representation of a periodically poled nonlinear structure 203. The structure has alternating domains 203 and 205, wherein the sign of the respective polarization vectors 204 and 206 alternate. The preferred separation of alternating domains are discussed by J. A. Armstrong, N. Bloembergen, J. Ducuing and P.S. Pershan in "Interaction Between Light Waves in a Nonlinear Dielectric," Phys. Rev., 127, 1918, 1962. The polarization in a domain of the structure 201 can be poled or switched by applying the sufficient bias voltage across the top surface and the bottom surface of the structure 201 which is normal to the polarization vectors 204 and 206, viz. the coercive field times the distance 209. Coercive field

value for Ferroelectric materials are in the range of about 10V/mm to 20 KV/mm

Figure 3 is block diagram outlining the method for making a periodic domain Ferroelectric structure in accordance with the instant invention. In the step 301 a Ferroelectric material is provided. The Ferroelectric material is either a high or a low coercive Field Ferroelectric, but is preferably a material that is substantially formed from $LiNbO_3$, $KTiOPO_4$ or $LiTaO_3$ and exhibits a coercive field value such that the material exhibits a spontaneous reversal of the local polarization with a change in temperature in the range of 0.1 to 40 degrees. In the step 303, conductive layers are provided on opposite surfaces that are substantially normal to the polarization vector axis. The conductive layers are formed from a conductive polymer, a metal or a salt composition material. According to the preferred embodiment of the invention, the conductive layers are formed from a mixture of polyaniline salt, n–Methyl pyrrolidone and Isopropanol, available under the name of ORMECON™ D-1000 manufactured by Ormecon Chemie GmbH & Co. KG, Ferdinand-Harten-Str. 7, D-22949, Ammersbek, Germany.

In a further embodiment of the instant invention the conductive layer includes a conductive polymer or a salt composition material in contact with the low coercive field Ferroelectric material and a metal deposited on top of the conductive polymer or a salt composition material. In accordance with this embodiment, it is preferable that the metal is not in direct contact with the low coercive field Ferroelectric material because some metals may react with the low coercive field Ferroelectric material and modify the electrical and/or optical properties of the material.

After the conductive layers are provided in the step 303, then in the step 305 a mask is formed on one of the conductive layers. The mask is preferably provided using lithographic techniques and using lithographic materials. A portion of the conductive layer on the top surface of the Ferroelectric structure is coated with a photo-resist. After the photo-resist is coated on the top conductive layer, the photo-resist and the structure is thermal cycled in accordance with the manufacturer's recommendations. The photo-resist is then exposed with a suitable light source according to a predetermined pattern and developed to form the mask. After the mask is provided in the step 305, then in the step 307 a single domain structure is formed. The single domain structure is formed by applying a sufficient bias voltage to each of the top and the bottom

conductive layers to pole the polarization vectors in one direction. The voltage applied across the conductive layer on the top surface and the conductive layer on the bottom surface is equal to or greater than the coercive field times the thickness of the structure.

Once the single domain structure is created in the step 307, then a conductive material is applied to the structure in the step 308 and the structures may be stored in the step for processing at a later time. In accordance with the embodiment, prior to the step 311 of removing a portion of one of the conductive layers, in the step 312 the conductive material on the sides of the structures shorting the top and bottom conductive layer is removed to place the top and the bottom conductive layers in electrical isolation. Either after the step 307 or the step 312, in the step 309, portions of the conductive layer are removed such that the conductive layer substantially replicates the mask and leaves a conductive domain template on the top surface of the Ferroelectric structure.

In the case where the initial domain structure (e.g. the starting material) is highly random with head-to-head domains in the body of the material, a single domain structure may be obtained by increasing the electrical conductivity of the material during poling through heating. Preferably, the material is heated to temperatures in a range of 100 and 200 degrees Celsius. The sign of the applied voltage then can be reversed several times during poling at these elevated temperatures in order to help eliminate the head-to-head domains.

A periodic domain structure is formed in the step 311 by applying sufficient bias voltage across the conductive template on the top surface and the conductive layer on the bottom surface of the structure that is equal to or greater than the coercive field times the thickness of the structure and biased in the opposite direction to that of the bias voltage applied in the step 309.

Figure 4a-g illustrates the steps for making a periodic Ferroelectric domain structure according to the preferred embodiment of the invention. Referring to Figure 4a, the Ferroelectric structure 401 is coated with conductive layers 420 and 421 on the top surface 405 and bottom surface 403. The structure 401 is preferably a low coercive field $LiNbO_3$ and $LiTaO_3$, as described above and the top surface 405 and the bottom surface 403 and 404 correspond to surfaces which are normal to the vectors of polarization 406 and 407.

Now referring to Figure 4b, on top of the conductive layer 420 a layer of photo-resist 430

is provided and cured. In accordance with an embodiment of the invention, the conductive layer 42 comprises a conductive polymer in contact with the surface 403 and 404 of the structure 401 with a second conductive layer formed from a metal deposited on the top of the conductive polymer. The embodiment is particularly useful when the polymer exhibits low conductivity. Thus the metal layer is provided to enhance the conductivity during domain poling but does not contact the surface 403 and 404 of the structure which leads to alterations of the electrical and optical properties of the resultant patterned structure. Also during the curing of the photo-resist layer 430, the side surface 402 and 402 may be coated with a conductive layer to place the layers 420 and 421 in electrical communication which helps reduce charging during the curing process. The conductive layer on the side surface (not shown) is removed prior to generating the single domain structure illustrated in Figure 4d.

Now referring to Figure 4c, the photo-resist layer 430 is exposed with an appropriate light source to generate exposed areas 431 and unexposed areas 438 of the photo-resist layer 430. The photo-resist layer 430 is then developed to remove the exposed areas 431 of the photo-resist layer 430 resulting in the formation of the mask 433 over the conductive layer 452, as shown in the Figure 4d.

Still referring to Figure 4d, a bias voltage is applied to the conductive layers 420 and 421 to generate a sufficient electrical field within the structure 401 such that the signs of the polarization vectors 406 switch signs 406' and align in one direction. The exposed portions of the conductive layer 420, which are not coincident with the mask 433, are then removed to form the surface 404 of the single domain 401' structure resulting in a conductive domain template 420' which is patterned similar to the mask 433 within typical processing parameters of lithographic techniques.

Referring to Figure 4e, a conductive layer 425 is preferably applied to side surfaces 402 of the wafer 401, such that the conductive layers 420 and 421 are placed in electrical communication. This helps to reduce the surface charging and the formation of micro domains. The structure then may be stored for an extended period of time without significant charging.

Referring to the Figure 4e, the conductive material is removed from the side surface 402 to place the top 420 and the bottom 420 conductive layers in electrical isolation. Portions of the

layer 425 are removed. The bias voltage is then applied to the conductive domain pattern template 420' and the conductive layer 421 in order to generate a sufficient electrical field within the structure such that the polarization vectors 407 between the template 421' and the conductive layer 421 change signs 407". The structure 401" is now periodically patterned with alternating signs of polarization throughout the structure. Preferably, the structure 401" is periodically patterned with domains that are spatially modulated by a distance corresponding to a coherence length such that the structure is useful as a QPM structure in a harmonic generator apparatus. Alternatively, non-periodic domain structures can be fabricated according to the needs of the particular application.

After the structure 401" is formed, then the conductive coating 421, the mask 433 and the conductive domain template 420' are removed and the domain patterned Ferroelectric structure 401" is ready to be coupled with a light source in the harmonic generator apparatus. Alternatively, the structure 401" is coated with protective layers 440 as shown in Figure 4g. Having described the preferred method of patterning a Ferroelectric material, Figures 5-6 are used to illustrated the additional advantage of using low-coercive field Ferroelectric materials in combination with the patterning method described above to make quasi-phase matching structures.

Figure 5 shows schematic view 500 of a patterning fixture for patterning high coercive field Ferroelectric material 501. Arcing can occur between a conductive layer on the top surface 502 and a conductive layer on the bottom surface 508, when electric fields as low as 3 kV/mm are applied. Thus the patterned conductive portions 503, 505, 507, 509 and 511 on the top surface 502 of the material 501 are often required to be significant distances D_1 and D_2 from the edges 504 of the material 501 to prevent arcing between conductive the portions 503, 505, 507, 509 and 511 on the top surface 502 and the conductive layer (not shown) on the bottom surface 508, when a poling voltage is applied from the voltage source 520. A second disadvantage to using high coercive field Ferroelectric materials to make quasi-phase matching structures is that the conductive patterned portions 503, 505, 507, 509 and 511 often need to be placed in electrical conductivity through connections 515 provided in a separated processing step, such as applying a liquid electrolyte between the conductive patterned portions 503, 505, 507, 509 and 511.

Further, because the top surface 502 of the material 501 is under utilized, for the reasons described above, suitable contact points 517 for the voltage source 520 is limited and a special fixture and procedure can be required for each different patterned structure produced.

In contrast to Figure 5 and the procedures outlined above, Figure 6 shows a schematic view of a patterning fixture 600 for patterning a low coercive field Ferroelectric material 601. In the above example, arcing around the edge of the wafer is due to the low dielectric strength of air, which is approximately 3kV/mm. As explained above, high coercive field Ferroelectrics require special fixtures and require that D_1 and D_2 are large. Low coercive field Ferroelectrics require fields that are less than 3kV/mm to pole the domains and, therefore, can permit for the use of conductive layers 602 and 608 which go to, or near to, edges 604 and 604' of the wafer 601, while still reducing the chance of arcing when a poling voltage is applied. Also, because a greater area of the top surface 602 is utilized, the contact point 617 for the voltage source 620 can be almost anywhere that there is conductive material and a special fixture and procedure is not required for each different pattern structure produced.

The present invention has been described relative to a preferred embodiment. Improvements or modifications that become apparent to persons of ordinary skill in the art only after reading this disclosure are deemed within the spirit and scope of the application. Specifically, the present invention is for providing domain patterning of any type of Ferroelectric materials including high coercive field Ferroelectric materials and composite Ferroelectric materials. The periodic domain patterned structures of the instant invention are useful in any number of optical, and electrical and acoustic devices including, but not limited to, waveguides and harmonic generator devices.